

A SIMPLE LIGHT ELEMENT X-RAY SPECTROMETER*

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The long wavelength x-ray region falls naturally into two parts: the shorter radiations between ca. 2 Å. and ca. 80 Å. which can be diffracted in depth by crystals and pseudocrystals, and the longer rays which, like the extreme ultraviolet, must be diffracted with ruled gratings. This entire part of the spectrum was mapped photographically¹ a generation ago; the renewed attention it is now receiving is due to several factors: (1) the desire to extend practical x-ray spectroscopy to the light chemical elements, (2) the improvements in x-ray technique that make this feasible, (3) the discovery of these x-rays in space beyond the earth's atmosphere and (4) the new information they can give about chemical combination.

The very high absorption of long x-rays in matter, including air, requires that their measurement be carried out in vacuo. In the earlier extension of x-ray spectroscopic analysis to

elements lighter than iron ($\lambda_{K\alpha} = 1.93 \text{ \AA.}$) x-rays traversed a column of helium or hydrogen but such helium-path instruments² were soon replaced by vacuum spectrometers. Absorption in commercial vacuum spectrometers is, however, already considerable for the $\lambda = 7.1 \text{ \AA.}$ characteristic of silicon, and it rapidly becomes prohibitive for elements of still lower atomic number. Over the last few years difficulties in the way of a further extension of spectroscopy to these and lighter elements have been solved and several forms of apparatus produced for quantitatively recording the K spectra of elements as light as boron ($\lambda = 69 \text{ \AA.}$). Most have been expensive to build and complicated to keep in operation. In this paper we describe the relatively simple spectrometric set-up we have developed for routine work in this region.

A major impediment to the x-ray analysis of the light elements has been the very low efficiency with which their characteristic x-rays can be excited by fluorescence. Other problems to be solved have dealt with the kind of crystal analyzer and detector to employ. No crystals suitable for spectrometry are available to diffract x-rays longer than ca. 25 \AA. ; extension to longer wavelengths has only recently become feasible through the demonstration that multi-layers of fatty acid salts, as made many years ago by Langmuir and Blodgett³, diffract these x-rays as well as single crystals

would be expected to do. Suitable detectors have resulted from finding a window material thin enough to pass very long x-rays while remaining strong enough to support an atmosphere's difference in pressure. Spectrometers now built for work in this region are in substantial agreement as to the "crystal" analyzers and detectors they employ; the unique feature of the instrument described here lies in the way its characteristic radiations are produced. The inefficiency of fluorescent excitation for the light elements can of course be more or less successfully countered by using an unusually powerful x-ray tube operated at low voltage. An example is the Henke-type tube as manufactured by Philips; it normally operates at 10 KV with a power input of ca. 3 KW. The window of such a tube is so thin and fragile that constant pumping is necessary; the equipment for doing this, together with the tube itself and its large stabilized power supply, make the installation an expensive one.

When, several years ago, we began to develop a soft x-ray spectrometer, a different approach was made to the problem of producing a suitable x-ray source. Measurements of fluorescent yields, made at the time⁴, convinced us that this type of excitation should be avoided. Direct electron bombardment has the desired efficiency but nonconductors cannot be made the anode of an x-ray tube that must operate in a

stable fashion. The charge they acquire results in a constantly fluctuating current and x-ray output, and many samples decompose rapidly under intense electron bombardment. It was found⁵, however, that these difficulties could be eliminated by using a "windowless" tube⁶ having the specimen as secondary target. Its characteristic x-rays are efficiently produced, mainly by electrons scattered from the primary target (the anode), without tube instability or a disturbing decomposition of the sample.

Such a windowless tube will operate with either a hot or a cold cathode. Experience has led us to prefer the latter, and the apparatus to be described is operated in this fashion. There were several reasons for such a choice. A generation ago gas tubes were commonly employed for x-ray diffraction because commercial tubes with the desired targets were not available, and because, in contrast to hot cathode demountable tubes, their targets remained remarkably free from contamination. This purity of spectral output is equally important for spectroscopy. Another outstanding advantage of the cold cathode tube for our purposes is the fact that only a simple fore pump is needed to produce its operating pressure of ca. 20 microns, and samples can be changed with little loss of time. Many years ago the senior author⁷ developed a gas tube for x-ray diffraction which now has proved

stable enough for the more exacting demands of quantitative spectrometry.

Two instruments have been built around such a tube, one using the Philips vacuum spectrometer as a basis, the other the Philips curved crystal spectrometer as supplied for the electron probe. A brief description of the first has already been published⁸. The second is described here. Each has advantages, and disadvantages. For the latter instrument, the chief disadvantages are the small angle 2 θ that can be reached and the lack of a dual crystal holder. The vacuum spectrometer meets both objections but its proportional counter and associated cathode follower are poorly adapted to the measurement of very long wavelengths, and vacuum problems with the spectrometer itself have made it more difficult to maintain a constant output through the tube.

The instrument described here (Fig. 1) is substantially that used in a recent survey of long wavelength L and M spectra^{9,10}. The tube (A) differs from its diffraction forerunner only in a changed distribution of entrance and exit ports and the addition of a specimen chamber (B). It could undoubtedly be made more up-to-date, notably through the replacement of brass in the body and of glass in the cathode portion. This has not yet been done because the performance

of the old design has been adequate for our purposes.

The specimen as secondary target is a compressed pellet or metallic slug one inch in diameter and of a convenient thickness. The present design of specimen chamber yields a beam of scattered electrons impinging on a small area of the sample which can be moved vertically while under vacuum with a screw (C) to ensure maximum peak intensity. Previous work⁴ has shown that the efficiency of characteristic x-ray production in a windowless tube is not strongly dependent on the material of the primary target (the anode). The results illustrated below were obtained with a target of copper; somewhat greater spectral intensities would have resulted from the use of gold, platinum or titanium.

A constant x-ray output is of course essential for quantitative spectrometry. Since the emitting anode (D) of a gas tube remains clean, this constancy is attained if the voltage and current across it do not vary. In our installation the wide voltage fluctuations in the power lines have been controlled with a G.E. Model 9X92Y3022 voltage stabilizing transformer. A satisfactory x-ray output has been achieved by using a fast pumping system and a Granville-Phillips Series 213 automatic pressure controller to provide a steady current through the tube. The vacuum line from the oil pump should be short, straight and of adequate bore; in

the outfit shown in Figure 1 it is 2" in diameter. The Welch Model 1397 oil pump is perhaps larger than necessary, but with it both tube and spectrometer are simultaneously reduced to operating pressure in less than one minute. Air, oxygen or argon is fed to the leak of the controller (E) at a constant pressure (of ca. 2 lbs./sq.in.) chosen so that in operation the valve will be partly open and thus able to react smoothly to changes in tube current. These are detected by connecting the control unit of the leak across the milliammeter of the high voltage power supply. Figure 2 reproduces the initial and terminal portions of traces of the peak intensities of the carbon ($\lambda = 45 \text{ \AA.}$) and aluminum ($\lambda = 8.3 \text{ \AA.}$) $K\alpha$ lines recorded over a period of about one hour. They demonstrate the short and long time stability of x-ray spectral output routinely obtained with this experimental arrangement.

The efficiency of characteristic x-ray excitation is such that power through the tube is normally less than 200 watts. For long wavelength excitation the voltage should not exceed 20 KV and hence only a modest and inexpensive selenium rectified power supply is required. The apparatus of Figure 1 employs one manufactured by Universal Voltronics Corporation. The small power consumption means that the body and target of the tube are easily water-cooled and that heat developed in the high voltage cathode (F) is adequately dissipated by

blowing (G) a small current of air against its fins. No cooling of the specimen chamber is needed.

In windowless tube operation it is essential to prevent any scattered electrons from reaching the detector (H) whose very thin window is as transparent to them as to the x-rays. Most are excluded from the spectrometer by placing between it and the tube a wide slit lined with Alnico magnets; a narrower slit of the same magnets (I) mounted in front of the counter window excludes the few that escape this first trap. Both are needed to establish the low background shown in our spectra.

With the quadrant spectrometer the diffracting crystal (J) can be used either flat or curved. Curving enhances the spectral intensities with stearate pseudocrystals as well as with mica but adequate intensities are obtained without curving. A wider choice of crystals is possible if flat ones are used and they are more quickly exchanged; for these reasons we routinely use all our crystals flat. For analysis of the elements Si, Al, Mg and Na we prefer potassium acid phthalate (KAP) to mica since its peaks are both more intense and farther apart. Because of the small angular reach of the quadrant spectrometer lead stearate pseudocrystals must be used to measure wavelengths longer than those of Na ($\lambda = 10 \text{ \AA.}$).

It has not been difficult to prepare suitable stearate

multilayers with a simple manually operated Langmuir trough, though lack of automation makes the process tedious. At first we were uncertain about the durability of these pseudocrystals. Their surfaces must be kept scrupulously clean without ever being touched and, like organic crystals used as gratings, they gradually suffer radiation damage. They are particularly susceptible to electron impact. Nevertheless we have used them with success over prolonged periods and they do not seem to deteriorate on storage. The spectra shown in this paper were made with a multilayer grating at least two years old.

The detector (H) is a flow counter of our own construction similar to that employed in the Philips probe. After passage through a Tenelec Model 100B preamplifier (K) its output enters one of the circuit panels conventionally used in x-ray spectroscopy. Its window is of stretched polypropylene which we have found much more transparent than the thinnest available Mylar and yet sturdy enough so that replacement is rarely required. The usual P-10 gas is employed for measuring sodium and heavier elements, but longer wavelengths are better measured if helium replaces argon. After investigating several compositions, we have selected a 50-50 helium-methane mixture for routine use. A counter fed with it at atmospheric pressure functions proportionally for the

longest radiation this spectrometer can record with an impressed voltage not exceeding 2800 volts.

The performance of this instrument can be judged from the carbon data of Figure 2, obtained from a sample of graphite when the power input was 5 MA at 10 KV. This peak intensity of ca. 5,800 c/s thus corresponds to an efficiency of 116 c/s/w; higher efficiencies have been obtained with other pseudogratings. Though one would probably never measure aluminum with a stearate grating, the intensity of its higher order reflections, as shown in Figure 2, is noteworthy. The advantage of windowless tube excitation is made apparent by the fact that the fluorescent yield from light elements measured with a conventional vacuum spectrometer is often more than a hundred times less.

The unchanging height of the aluminum peak of Figure 2 over a prolonged period shows not only that the x-ray output of the tube has remained constant but that there has not been any massive contamination of the specimen. It has been important to make similar measurements on weak peaks to find out if there has been even a slight contamination or alteration in the specimen. This has been done with carbon-containing samples since they would be expected to be most easily damaged by the electron beam. We have found that if carbon is present in a stable form, as for instance a carbonate

mineralizing a fossil bone, there will be no perceptible change in height of the carbon peak during an hour of irradiation; on the contrary, the measured amount of oxidizable carbon, such as the organic residue in a fossil or the carbon in a steel, may very gradually (see Figs. 3 and 4) diminish on prolonged irradiation provided oxygen has been fed into the tube. When argon is employed, a sample rich in carbon develops a darkened spot presumably due to reduction by the bombarding electrons. Since any carbon thus produced will not escape from the specimen, it is sometimes preferable to use argon.

The typical spectral data that follow illustrate results obtained when using this spectrometer to measure light elements present in large or small amounts in pure compounds, steels, rocks and fossils.

The carbon peak of Figure 3, from a pressed sample of (ethylene dinitrilo) tetraacetic acid, EDTA, is typical of those given by compounds rich in carbon; its continuing unaltered height (left portion of the figure) demonstrates the validity of the measurement. A carbon steel gave the less intense carbon and nearby second order 1λ peaks of iron reproduced in Figure 4; we have found it convenient to employ this iron peak as a built-in internal standard for evaluating the carbon. Another example of the spectra provided by

low-carbon samples is shown in Figure 5; in work with such a fossil bone, overwhelmingly apatite in composition, the first order oxygen $K\alpha$ peak, at the right, supplies the internal standard. Though it is evident from the last two figures that small amounts of light elements can be detected without difficulty, special precautions must be taken if quantitative results are sought. It is a consequence of the extreme absorption of long x-rays that all recorded radiation originates very close to the specimen surface. This must therefore be smooth and scrupulously clean; the grease of a fingerprint or a few embedded grains of a polishing agent can vitiate an analysis. Matrix and particle-size effects are particularly important and internal standards probably cannot be avoided.

The greater sensitivity that can be attained by employing this spectrometer to analyze those lighter elements still within the reach of conventional fluorescent spectrometry will be illustrated by measurements on an igneous rock and a fossil extract. Representative spectra of silicon, aluminum, magnesium and sodium obtained from a standard rock (B.S.#4985, Deccan trap) using our spectrometer equipped with a potassium acid phthalate crystal are shown in Figure 6. Their intensities, compared in Table 1 with those furnished by mica and gypsum, indicate the superiority of the phthalate. This

specimen, measured in the conventional vacuum spectrometer equipped with an EDDT crystal, gave a silicon peak height of 19 c/s/100w (instead of 1460 c/s/100w). For aluminum the comparable peak values were 352 c/s/100w (see Table) and 4 c/s/100w. The phosphorus and carbon peaks of Figure 7 were supplied by the presumed phospho-lipid residue extracted from a fossil bone. They clearly demonstrate the organic nature of the residue and the considerable amount of phosphorus associated with it. In the commercial spectrometer operated at low voltage (20-30KV) to obtain maximum fluorescent yield, this sample gave a phosphorus peak of a few counts per second with a far less favorable peak-background ratio.

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Table 1

Peak Intensities from Deccan Trap

<u>Element</u>	<u>% Composition</u>	<u>c/s/100w KAP Crystal</u>	<u>c/s/100w Mica</u>	<u>c/s/100w Gypsum</u>
Ca	6.51	84	40	82
K	0.65	48	16	20
Si	23.23	1460	480	770
Al	6.62	352	114	208
Mg	3.40	100	32	52
Na	1.70	36	14	—

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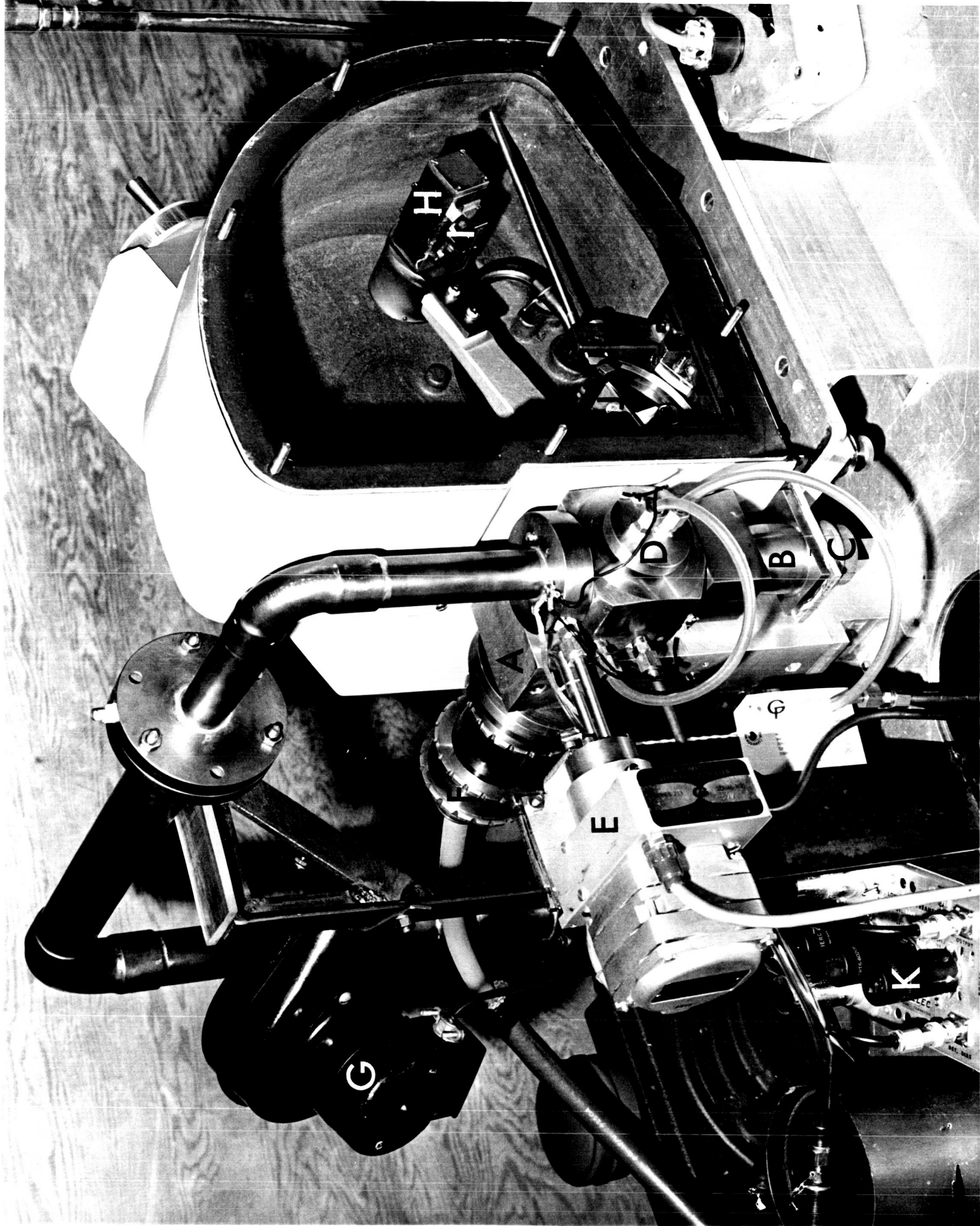
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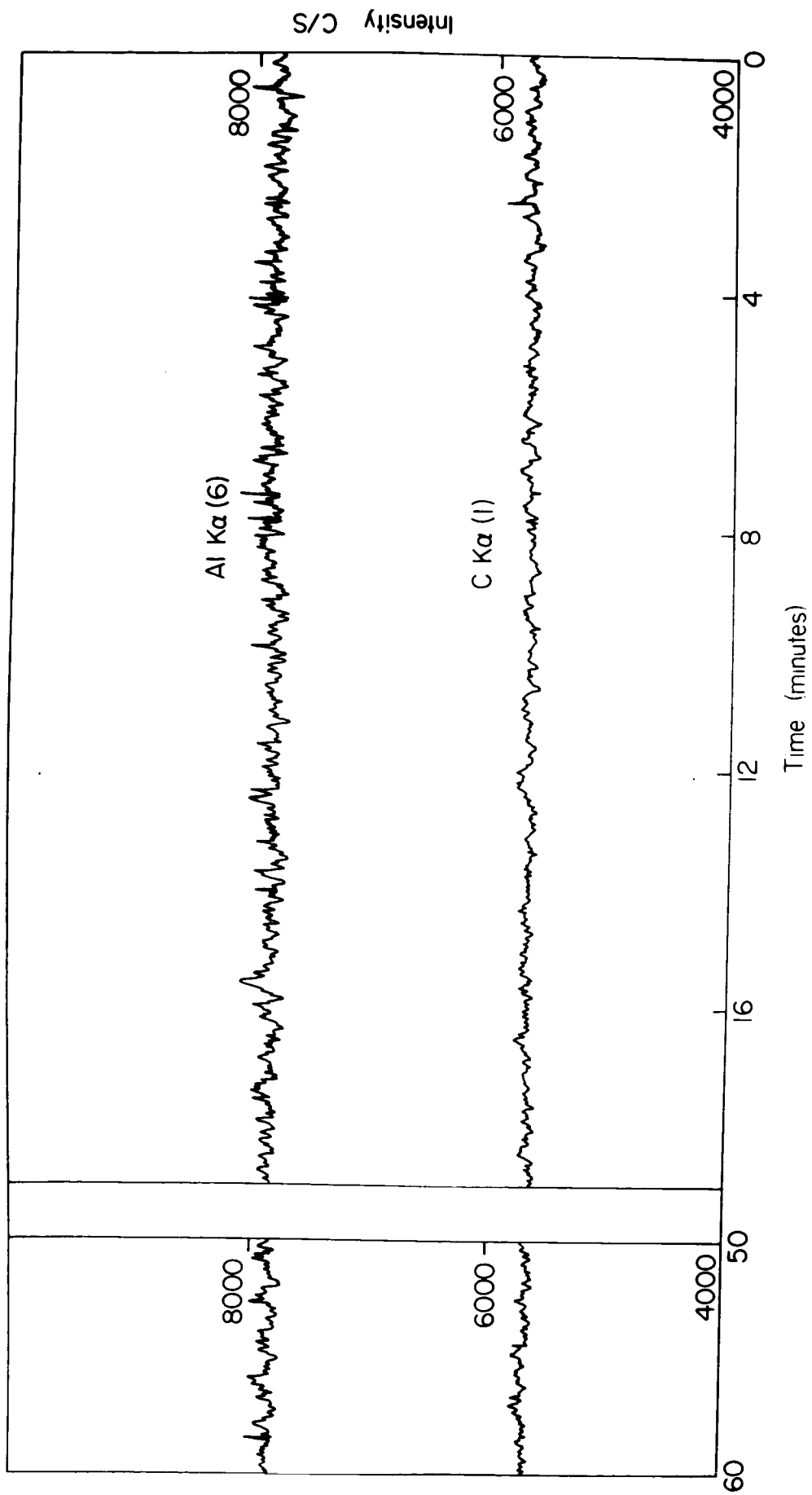
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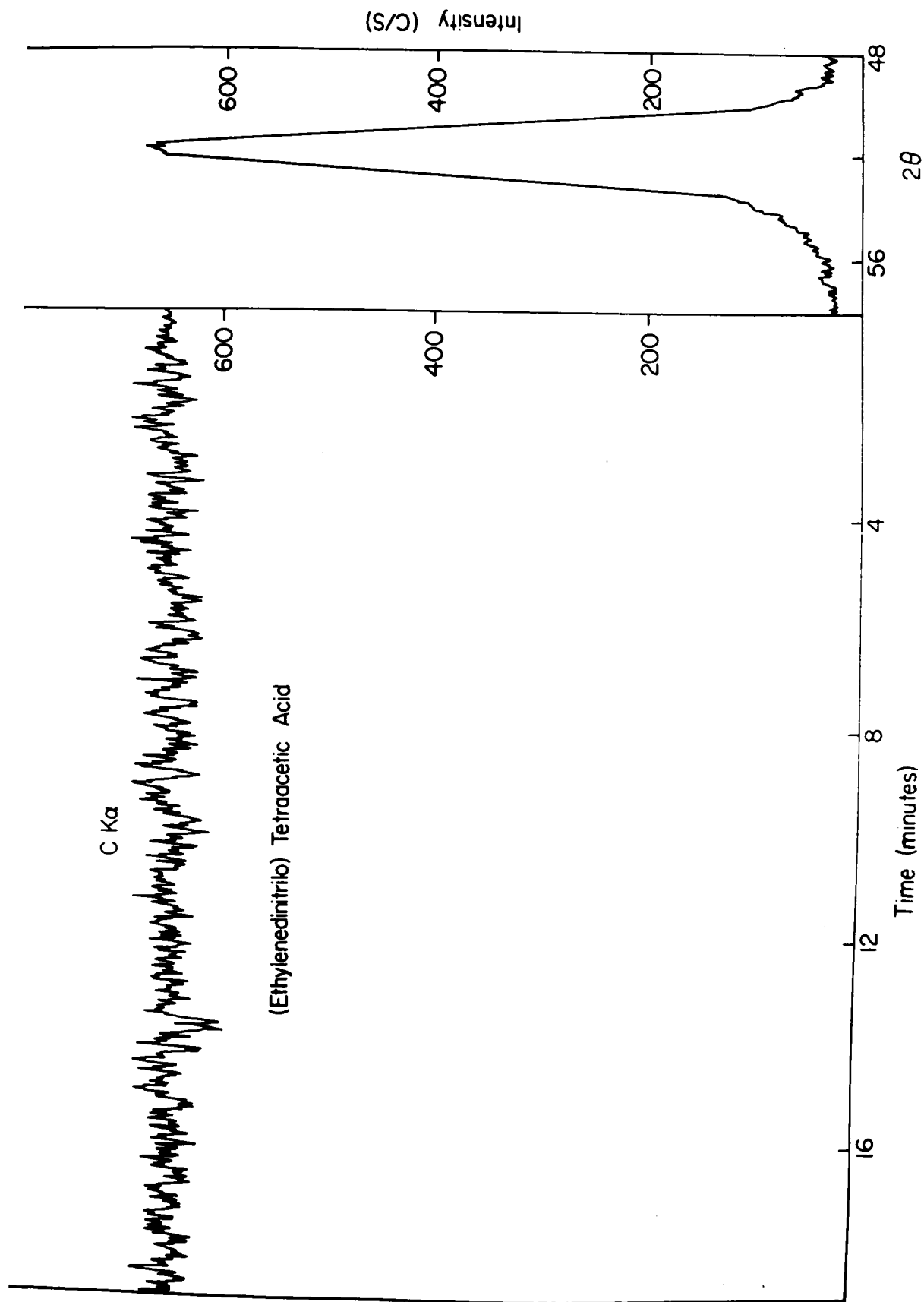
- Figure 1. A photograph of the windowless soft x-ray spectrometer. Lettered parts are identified in the text.
- Figure 2. A time-vs.-intensity plot of the peak heights of the carbon $K\alpha$ and aluminum $K\alpha$ (6th order) reflections with 50 watts through the x-ray tube. The plot for the full hour was too long for reproduction but the omitted portions were indistinguishable from those shown; the heights did not change measurably.
- Figure 3. To the right, the recorded carbon peak from a compressed sample of EDTA, and to the left, a time-vs.-intensity plot of this peak. Tube power = 50 watts (5 MA, 10 KV).
- Figure 4. The carbon and Fe $L\alpha$ (2nd order) peaks from a small (0.5 inch diameter) specimen of high carbon steel. The surface was freshly exposed by taking a thin cut on the lathe with a cleaned tool, without subsequent polishing. Tube power = 50 watts.
- Figure 5. The carbon and oxygen peaks from a slab of fossil bone and, on the left, a time plot of the carbon peak height. The unchanging height of this small peak shows that neither was the carbon of the specimen burned nor was a detectable deposit formed during the irradiation. Tube power = 50 watts.

Figure 6. Peaks for silicon, aluminum, magnesium and sodium recorded from a powdered sample of igneous rock (B.S.#4985). Note the relatively low backgrounds. Tube power = 50 watts.

Figure 7. The phosphorus (KAP crystal) and carbon (stearate pseudocrystal) peaks from a dried methyl chloride solution of a fossil residue. Weight of initial fossil sample = 1 gm. Tube operated at 5 MA, 15 KV.







High Carbon Steel

